LA-UR-97-1384

Title:
A Precise Method for Determining the CO_2 Content of Carbonate Materials

Author(s):
Donald L. Pile, Alana S. Benjamin, Klaus S. Lackner, Christopher H. Wendt, and Darryl P. Butt

Los Alamos
NATIONAL LABORATORY

A Precise Method for Determining the CO_2 Content of Carbonate Materials

Donald L. Pile*, Alana S. Benjamin*, Klaus S. Lackner**, Christopher H. Wendt**, and Darryl P. Butt*[†] ,
Materials Corrosion and Environmental Effects Laboratory
*Materials Science and Technology Division and
**Theoretical Division
Los Alamos National Laboratory
Los Alamos, NM 87545

Introduction

A program undertaken in our laboratory assessed the feasibility of reacting CO_2 gas with abundant raw materials to form stable carbonate materials as a method for CO_2 disposal (*1-4*). Part of these studies required a quick and simple, yet accurate, method for the analysis of the carbonation product, something for which the literature was wanting. A published ASTM standard for the determination of carbon dioxide in limestone employs the weight change of a sodium hydroxide-coated silica absorbent (*5*). This standard involves the painstaking efforts of keeping the system free of atmospheric carbon dioxide and the measurement of possibly very small mass changes. Papers in this *Journal* describe the collection of gas from a reaction which is then volumetrically measured and used in calculations (*6,7*). These procedures arrive at the number of moles of the gas through the ideal gas law, using the nominal volume. Another method of gas collection employs a manometer and calculates the number of moles by calculating the partial pressure of the gas of interest, measuring the volume, and using the ideal gas law (*8*). The eudiometry method of carbonate analysis presented by Dudek (*6*) is similar to our method. However, this method uses a different measurement and calculation procedure that results in, reported, larger errors than we could tolerate.

Therefore, the following procedure was developed and refined to improve the accuracy of measuring the CO_2 content in carbonate materials. In our experiments, a simple apparatus was

---

[†] Point of contact.

designed to measure the volume change originating from CO_2 gas formed by a reaction of the carbonated sample and a solution of hydrochloric acid. An equation was derived to accurately arrive at the volume due to evolved CO_2 and corrected for pressure and other effects. The mass was calculated by multiplying this volume by the gas density under ambient conditions.

Students with the appropriate background, typically honors Freshmen and higher, should be able to derive the equations, with some guidance, so that they understand the underlying principles in the measurement and the additional corrections in the volume determination. This experiment could be introduced as an application of the ideal gas law and for determining the gas content of a mineral such as a carbonate. In the second case, the stoichiometry of unknowns, that evolve a certain known gas, could be determined, such as described in reference 6. In comparing the herein described procedure to more simple methods, the student should appreciate the need for refined measurements and fewer assumptions in calculations to obtain greater accuracy.

Design and Construction of Apparatus

The gas collection and measurement apparatus is easily assembled using components found in most general chemistry laboratories. A buret is modified by having a scientific glassblower cut off the stopcock end and attach it to the opposite end, then join a glass connecting tube, a few millimeters in diameter and crooked upwards, to the buret sidewall a few centimeters from the opening opposite the stopcock end (see Figure 1). Consequently, the scale numbers are read rightside up and increase in value from the stopcock end toward the opening. If no scientific glassblower is available to perform the glasswork, then a piece of glass tubing could be bent and inserted in the opening of an unmodified buret. However, readings of the buret must be made carefully since the scale would be upside down. The connecting tube should be calibrated for volume with 0.1 mL gradations. The supported buret is submersed in a large pool of water with its opening below the water surface and above, and not touching, the floor of the water dish so water flows freely between the pool and buret. The glass side tube is connected with flexible tubing to a glass tube inserted in one hole of a two-hole rubber stopper, which fits the reaction test

tube. The second hole in the rubber stopper accommodates the pipette used to measure and inject

the volume of acid solution onto the weighed carbonate sample at the bottom of the test tube. A

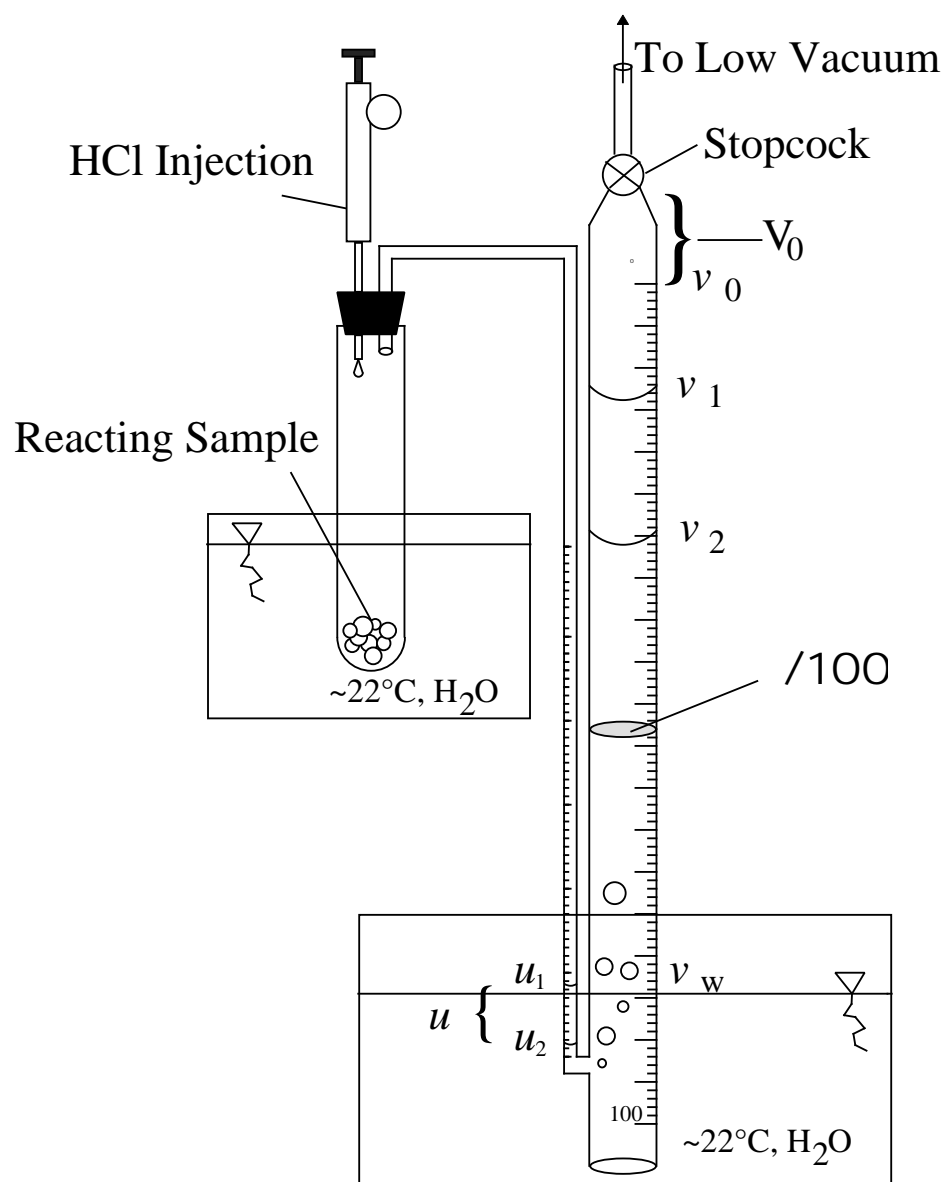water bath surrounding the test tube helps maintain a constant temperature.

Figure 1. Schematic diagram of gas collection and measurement apparatus. Labels are defined in the text.

Procedure

The general procedure involves dissolving the carbonate material and liberating CO_2 gas using an acid solution (6 M HCl is recommended). In the case of calcium carbonate the reaction is

$$CaCO_3(s) + 2HCl(l) \quad Ca^{2+}(aq) + 2Cl^-(aq) + H_2O(l) + CO_2(g)$$
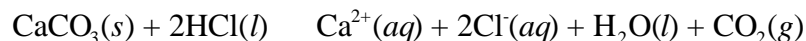
The evolved gas is captured and the change in gas volume measured. Relating this volume change measured with the buret to the mass of CO_2 evolved is accomplished using experimental measurements and system parameters in equations derived in the following section.

First, fill the large water dish to the water level on the buret, v_w, with distilled or deionized water. This water in short time will absorb carbon dioxide from the air to form carbonic acid. A small amount of a strong acid may be added to the water to keep it slightly acidic, thereby completely preventing dissolution of the CO_2 stream from the reaction test tube. (Most likely the water is saturated with CO_2 from the atmosphere and will be already slightly acidic.) Second, pull a low vacuum from the tube above the buret stopcock. A three-valve pipet bulb attached to the buret tip may be used to draw the vacuum. Open the stopcock to draw water from the pool up into the buret, then close it after adjusting the meniscus to an arbitrary reading level, v_1.

Place a small weighed-out sample of the carbonate material of mass $M_{carbonate}$ in the bottom of the reaction test tube. A powdered material has a high surface to volume ratio, enhancing the reaction with the acid. Fit the rubber stopper in the test tube opening. Pipette a known volume of hydrochloric acid, V_{HCl}, and insert the pipette into the second hole in the rubber stopper. Typically 2.0 mL of 6 M HCl is plenty to bring the reaction with approximately 0.1 to 0.2 g of sample to completion. Care should be taken to keep any acid from dropping onto the sample before the injection time. Place the test tube in a water bath for controlling the temperature of the reaction. These last connections and adjustments may have changed the pressures and volumes in the system. Therefore, after closing the system and before injecting acid, check the water levels, both the meniscus at v_1 and the bubble level in the side tube crook, u_1, and record these values.

Inject the acid and watch the plume of gas displaced by the CO_2 from the reaction flow through the feed tube and rise into the buret. Make sure that no gas escapes from the bottom of the buret. This happened occasionally with highly carbonated samples that released the CO_2 too fast. Gently shake the test tube to dislodge and dissolve any solid spattered on the side during the HCl injection. After a set time, at which no noticeable change occurs, read and record the meniscus of the water level in the buret, v_2. Also, note and record any change in the side tube bubble, $u = u_2 - u_1$. Since this bubble level in the side tube occurs after the gas evolution, it is more proper to associate this volume change, u, with the final buret reading, v_2. Subtract the u from the original v_2 to arrive at the adjusted v_2. (For example, shown in Figure 1 is a negative volume change, $u < 0$, which results from additional gas in the feed tube and can be thought of as gas that did not flow into the buret to give a larger gas volume above the water column. Note that the positions of u_1 and u_2 in Figure 1 are for illustration. The volume change u could also be positive.) There is a very slight, but negligible, error associated with this calculation since the volume of gas in the feed tube is at a different pressure than the pressure of the gas above the water column.

Obviously, any gas escaping through the buret opening at the bottom results in an under measurement of CO_2 gas. Smaller sample weights may be necessary if the reaction occurs too violently or if the u in the connecting tube is larger than about 1 mL. We found that large changes in u are frequently associated with rapid heating and subsequent cooling of a strongly reacting sample. The initial heating causes the gas to expand. This leads to an excess of gas flowing into the buret that eventually is compensated by water entering the side tube crook. Smaller samples generate less heat and are thus less prone to this problem.

In addition to the above measurements, record the ambient temperature, T_a, and pressure, P_a. Also, there is a necessary correction to be made experimentally with the system. Run an experiment on a sample, of same size, that does not give off gas, such as sodium chloride. The resulting volume change in the buret stems from the acid volume injected as well as some evaporation of the acid due to a vapor pressure of the acid solution in the test tube. This correction

is on the order of 0.1%. Additionally, this step will help compensate for the loss of volume due to sample dissolution. In subsequent experiments subtract this correction volume, V_c, from the change in gas volume. The V_c term is valid only for the experimental and atmospheric conditions under which it was determined. Use the experimental values in the equation to calculate the mass of CO_2, M_{CO2}, which is derived in the following section.

Derivation of CO_2 Gas Mass Formula

For calculating the mass of CO_2, an equation was derived from the ideal gas law, density equation and measured gas volume, and by applying correcting factors for the ambient conditions and pressure variations along the buret apparatus. Following are the equations and assumptions used in deriving the mass of CO_2 evolved and captured in the buret. First, the gas density is calculated for the local temperature and pressure. Next, the volume is determined from the changes in the buret reading and corrections for pressure and volume effects. The gas density is multiplied by the volume change due to the evolved gas (corrected to ambient conditions) to arrive at the mass of CO_2. All calculations assume CO_2 behaves as an ideal gas. (The experimental procedure relies on the CO_2 and air behaving as ideal gases, which for all practical purposes is true at atmospheric pressure.)

Determining Local Gas Density

The gas density is calculated from known values of the local temperature and pressure. The density of the gas can be calculated by dividing the molar mass, or formula weight, by the molar volume:

$$\rho_{CO2} = (44.01 \text{ g mol}^{-1})/V_m \tag{1}$$

The molar volume is obtained using the ideal gas law:

$$V_m = 10^6 \cdot RT_a/P_a \text{ cm}^3 \cdot \text{mol}^{-1} \tag{2}$$

where T_a is in K, P_a is in Pa, and the 10^6 factor is to convert from m^3 to cm^3. The unit Pa for pressure is used since it is an SI unit ($=N \cdot m^{-2}$). The appropriate conversions are necessary for

using other units. One can obtain the temperature using a thermometer and the local pressure using a barometer in the lab. Note that the pressure reported by the local weather station is corrected to sea level.

If less accuracy is required, one can assume room temperature, approximately 22 ˚C, and calculate the average atmospheric pressure from the known elevation of the laboratory; there is approximately a 10 Pa decrease in pressure for every meter above sea level where $P_a = 101325$ Pa, i.e., $P_a \approx 101325$ Pa - $(10$ Pa $m^{-1})$ (elevation).[1] For example at our lab's elevation of 2250 m and for 22 ˚C, V_m is 31,134 $cm^3 \cdot mol^{-1}$ and ρ_{CO_2} is 1.414×10^{-3} g·cm^{-3}.

Measuring Gas Volume

The buret serves to capture and measure the volume of gas generated. Two volume readings, v_1 and v_2, are made for the initial and final gas volumes in the buret, where $v_1 < v_2 < v_w$. The difference in these two readings will give a nominal volume. However, the individual readings are important in that the water levels they mark are dependent on the pressure as well as the volume of the gas above the water. The derivation of a comprehensive equation to calculate the ambient condition-corrected gas volume from measurements on the buret follows.

First, two other system-specific variables should be ascertained. The buret volume to height ratio (cm^3 m^{-1}), designated as γ, relates the volume of liquid per length of column. This ratio may be found by dividing the volume scale of the buret by the linear length of the buret scale. The volume V_0 (mL) accounts for the volume between the zero marking, v_0, and the stopcock. This volume may be measured by pipeting a known amount of liquid to fill the buret end. For our

---

[1] An expression for pressure as a function of height, at constant temperature, is
$$p = p_0 e^{-gz / RT_0}$$
where p_0 is the reference pressure, g is the acceleration of gravity, z is the difference in altitude (elevation), R is the gas constant (0.28704 J/g·K), and T_0 is the constant air temperature. See Dutton, J. A., The Ceaseless Wind. An introduction to the theory of atmospheric motion, McGraw-Hill, Inc., New York, 1976, p. 69 and p. 82.

system, and V_0 were determined to be 91.73 cm³ m⁻¹ and 7.0 mL, respectively; the water level of the pool on the buret scale, v_w, was set at 49.5 mL.

The height of the water column in the buret, h (m), is due to the hydrostatic pressure of the water in the buret, which is the difference between the pressure inside and outside the buret. The hydrostatic pressure equation is

$$p = \rho_{H2O} \cdot g \cdot h \tag{3}$$

where p is pressure (Pa), ρ_{H2O} is the density of water (1000 kg·m⁻³), and g is acceleration of gravity (9.8066 m·s⁻²). The ratio of the pressure of the gas trapped inside the buret above the water column to the ambient pressure is related to the ratio of water column heights by the equation:

$$P_b/P_a = (H - h)/H \tag{4}$$

where P_b is the pressure of gas (Pa) inside the buret, and H is the height (m) that would be achieved for the ambient pressure, P_a, acting upon the pool of water if the buret was sufficiently tall and the pressure above the column was zero, i.e., a vacuum. The variable h is the equivalent of the gas pressure inside the buret expressed in terms of a height of the water column. A check of the two extremes demonstrates the equation's validity: (*i*) at $P_b = P_a$, the measured height, h, is zero, and (*ii*) at $P_b = 0$, the measured height, h, would be H, which is the height of the water column for a hydrostatic pressure equal to the local pressure, which itself is dependent on the local elevation and weather conditions:

$$H = (P_a)/[(1000 \text{ kg·m}^{-3}) \ (9.8066 \text{ m·s}^{-2})] \tag{5}$$

As a good approximation, the density of water is 1 g·cm⁻³ for moderate temperatures near room temperature (25 ˚C) and the local atmospheric pressure. (Any change in liquid density due to dissolved gases and added acid is not accounted for here, but is a small effect.) For greater accuracy, one could easily correct for the pressure and temperature dependence of water density.

The volume to height ratio   converts measurements using the buret scale to the dimension of height used in equation 4. For example, the buret water height, h, can be obtained by the difference in buret readings at the water meniscus, v, and the water level, v_w, divided by the volume to height ratio,   :

$$h = (v_w - v)/ \tag{6}$$

For the case that hydrostatic pressure equals the ambient pressure (i.e., $P_b = 0$ and thus h = H), the water column volume is defined as v_H:

$$v_H = H \tag{7}$$

This term is used to simplify the pressure-dependent term in the derivation steps.

The volume of gas inside the buret, corrected for the local pressure, is

$$V = (V_0 + v) \ (P_b/P_a) \tag{8}$$

where V has units of milliliters. Substitution of equations 4, 6 and 7 into equation 8, yields

$$V = (V_0 + v) \ \{[v_H - (v_w - v)]/v_H\} \tag{9}$$

The initial gas volume reading is given by v_1, the final by v_2. Thus,

$$V_1 = (V_0) \ [(v_H - v_w + v_1)/v_H] + (v_1) \ [(v_H - v_w + v_1)/v_H] \tag{10}$$

$$V_2 = (V_0) \ [(v_H - v_w + v_2)/v_H] + (v_2) \ [(v_H - v_w + v_2)/v_H] \tag{11}$$

and

$$V = V_2 - V_1 = (V_0) \ [(v_2 - v_1)/v_H] + (v_2 - v_1) \ [(v_H - v_w)/v_H] + (v_2^2 - v_1^2)/v_H$$

$$= (v_2 - v_1)[V_0 + v_H - v_w + v_2 + v_1]/v_H \tag{12}$$

Since v_H is a function of pressure (= P_a /9806.6 from equations 5 and 7),   V can be rewritten as

$$V = (v_2 - v_1) \ (V_0 + P_a \quad /9806.6 - v_w + v_2 + v_1)/(P_a \quad /9806.6) \tag{13}$$

Equation 13 expresses the volume of gas generated in terms of the local pressure, apparatus parameters, and experimental measurements.

Mass of Evolved CO$_2$

As introduced earlier, the mass of CO_2 is found by multiplying the volume by the density of the gas, each at the proper pressure and temperature. The volume V, determined above in equation 13, is the gas volume under ambient pressure. A correction to the gas volume must be made to account for the volume of the hydrochloric acid injected, V_{HCl}. In our experiments V_{HCl} was 2.0 mL. Additionally, a correction volume must be subtracted to take into account any added vapor due to evaporation of hydrochloric acid solution as well as sample volume loss due to dissolution. This correction, V_c, is found by performing the experiment with a dissolvable material that does not evolve gas and, using equation 14, setting the mass of CO_2 generated to zero:

$$M_{CO2} = \rho_{CO2} \cdot (V - V_{HCl} - V_c) \tag{14}$$

All volumes are measured in milliliters and masses in grams.

Weight Percent CO$_2$

The percent CO_2 is found by dividing the mass of CO_2 by the mass of the reacting sample. The comprehensive equation for weight percent CO_2 is the combination of equations 1, 2, 13, 14 and the mass of the reacting carbonate sample, $M_{carbonate}$, as follows:

$$\% \, CO_2 = \frac{\dfrac{44.01 \, P_a}{10^6 \, R \, T_a} \, (v_2 - v_1) \left[1 + \dfrac{9806.6}{P_a}(V_0 + v_1 + v_2 - v_w) \right] - V_{HCl} - V_c}{M_{carbonate}} \times 100\% \tag{15}$$

The range of determinable CO_2 is dependent on the range in the buret, i.e., $v_2 - v_1$, and the sample size. In our set-up, $v_2 - v_1$ had a practical range of 49 mL and sample weights were typically 0.1 g, thus giving us the ability to calculate up to about 64% (by weight) CO_2. Of course, smaller sample sizes can increase this number.

Assessment of Technique

The accuracy of the technique can be assessed by performing a calibration experiment using chemicals of known carbonate content. The accuracy of a self-constructed apparatus will of course change from lab to lab. For illustration purposes, we mixed varying amounts of CaO and $CaCO_3$ powders and measured their CO_2 content. Figure 2 shows the results and statistics of these calibration experiments comparing the measured CO_2 content versus the nominal weight percent (i.e., assuming the CaO and $CaCO_3$ were perfect stoichiometric compounds). In reality, the CaO contained approximately 1.3% carbonate by weight, while the $CaCO_3$ was effectively 100% $CaCO_3$. The data gave a slope of 0.978, which is in statistical agreement with the predicted slope of unity (assuming the $CaCO_3$ and CaO are perfect stoichiometric compounds) and is in excellent agreement with the more relevant slope of 0.97 assuming the CaO contains 1.3% carbonate. As shown in Fig. 2, the standard error was 0.0108 for this small sampling set and for sample sizes of approximately 0.1 g. Figure 3 shows the residuals which generally were 1% or less. It appeared that the residuals were slightly greater at smaller CO_2 contents, which would be expected given the smaller evolved gas volume.
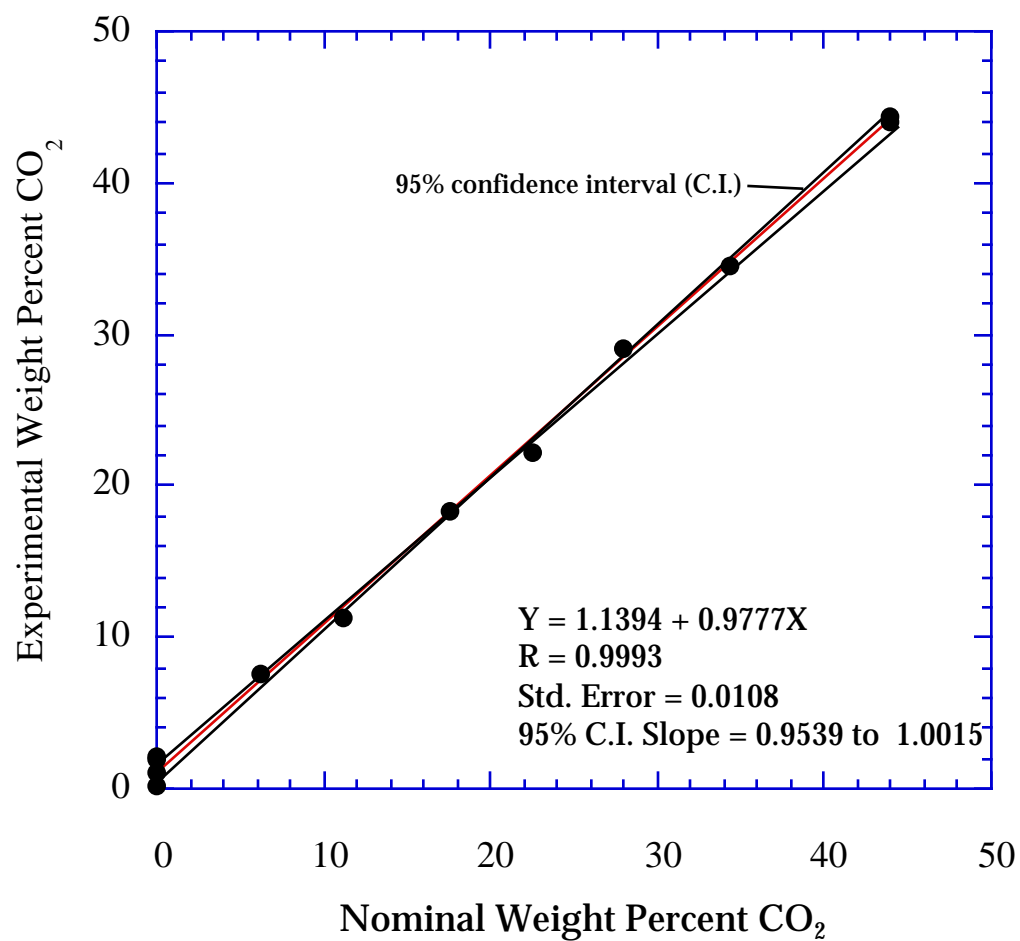
Figure 2. Calibration plot of experimental system using $CaCO_3$ and CaO powders and mixtures of the two. The measured values are plotted against the nominal compositions. The slope is slightly less than one due to carbonate impurity intrinsic in the CaO powder. Note that the sample size was 0.1 g.
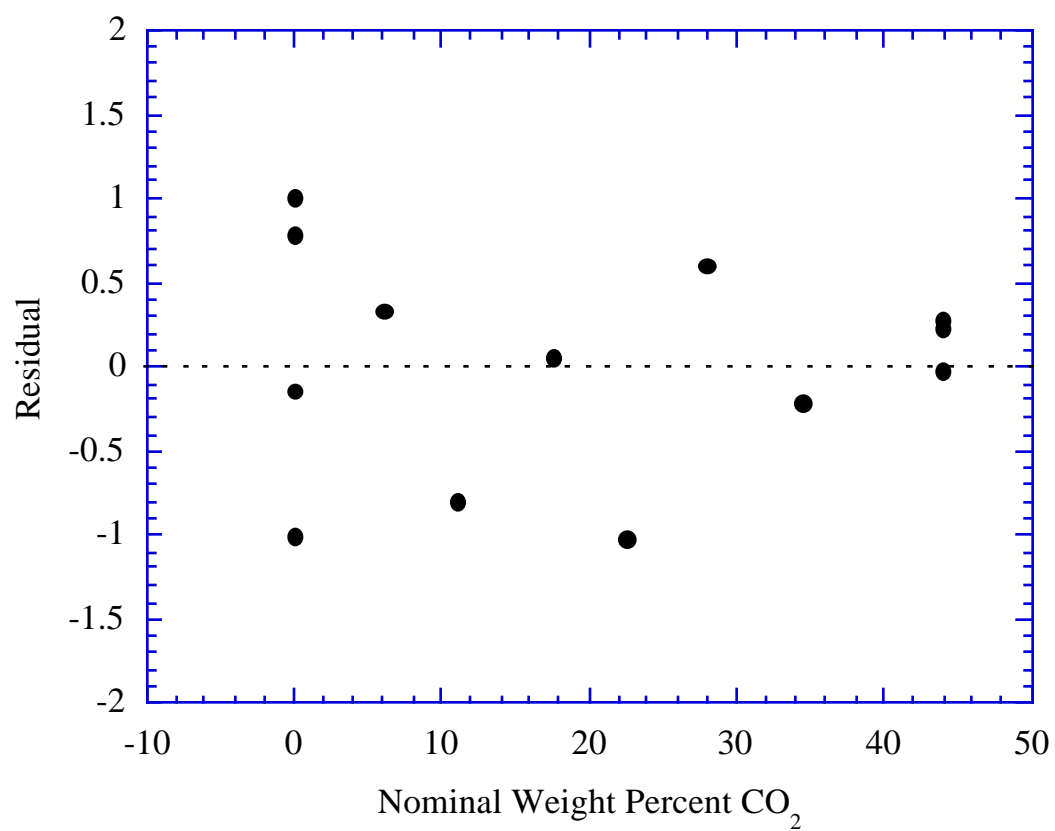
Figure 3. Residuals from linear regression of the calibration data shown in Fig. 2.

To reduce possible errors it is important to ensure that the system is sealed well. For example, the rubber stopper should form a tight seal with the test tube as should the pipette pump or bulb with the pipette. Also, powder that alights on the side of the test tube, although included in the sample mass, does not contribute to the CO_2 mass, leading to a lower measured CO_2 volume. Other precautions include those mentioned in the procedure section.

Sample Calculation

The following set of values is from an actual run for measuring the CO_2 content of a $Ca(OH)_2$ sample that was exposed to CO_2 at $800\,^\circ C$ for 1 hr. First the V_c volume correction term was determined using blanks of salt in place of the carbonate. The experimental values for the calibration are listed in Table 1. During the tests, the temperature was 25 $^\circ C$ and the pressure 77670 Pa. The water level, v_w, was at 49.5 mL. Our apparatus-specific variables   and V_0 were determined to be 91.73 cm^3 m^{-1} and 7.0 mL, respectively.

v_1	u_1	v_2	u_2	V_{HCl}
0.0	0.35	2.1	0.1	2.0
2.1	0.45	4.15	0.1	2.0
4.15	0.4	6.25	0.1	2.0

Table 1. Data obtained for the calibration runs with a salt blank instead of the carbonate.

As stated in the procedure section, the $u = u_2 - u_1$ is calculated and subtracted from the v_2 term to arrive at a corrected second buret volume reading. Then V_c is found by setting the % CO_2 term to zero in equation 15, yielding

$$V_c = (v_2 - v_1) \left[1 + \frac{9806.6}{P_a} (V_0 + v_1 + v_2 - v_w) \right] - V_{HCl} \tag{16}$$

and a value of 0.3 after rounding the average of the three results to the nearest 0.1 mL.

The experimental values for the carbonate testing are listed in Table 2. These values are used in the comprehensive mass percent CO_2 equation, equation 15, along with the V_c term calculated above, giving results of 39.7% and 38.1%. The difference between the two values is attributed to the inhomogeneity of the carbonated sample.

$M_{carbonate}$	v_1	u_1	v_2	u_2	V_{HCl}
0.1001	0.1	0.4	31.55	0.25	2.0
0.0996	0.3	0.4	30.45	0.25	2.0

Table 2. Data obtained for a $Ca(OH)_2$ sample that was exposed to CO_2 at $800^\circ C$ for 1 hr.

Conclusions

A simple analytical procedure was described that provides a means for determining the mass of CO_2 from a carbonate material. This approach is more rigorous than simply using nominal volume changes, resulting in accuracies better than 1%, depending on the design of the apparatus and accounting of environmental and system variables. This procedure can be extended to determine the gas content of other materials that evolve a certain gas upon dissolution. Furthermore, this experiment teaches and uses concepts of the ideal gas law and fluid mechanics.

References

1. Butt, D. P.; Lackner, K. S.; Wendt, C. H.; Conzone, S.; Kung, H.; Lu, Y.-C.; Bremser, J. K. *J. Am. Ceram. Soc.* **1996**, *79*, 1892.

2. Lackner, K. S.; Wendt, C. H.; Butt, D. P.; Sharp, D. H.; Joyce, E. L. *Energy* **1995**, *20*, 1153.

3. Lackner, K. S.; Wendt, C. H.; Butt, D. P.; Sharp, D. H. in proceedings of *21st International Technical Conference on Coal Utilization and Fuel Systems*, B. A. Sakkestad, Ed.; Coal and Slurry Technology Association: Washington DC, 1996; pp 133-144.

4. Lackner, K. S.; Butt, D. P.; Wendt, C. H. Los Alamos National Laboratory Technical Report, LA-UR-97-660, 1997.

5. "Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime," Designation: C-25-95, Section 22: "Carbon Dioxide by Standard Method", *1995 Annual Book of ASTM Standards*, Vol 04.01; ASTM: Philadelphia, PA, 1995; pp 21-22.

6. Dudek, E. *J. Chem. Educ.* **1991**, *68*, 949.

7. Burgstahler, A. W. *J. Chem. Educ.* **1992**, *69*, 575.

8. Basman, A. R.; Chorley, G. B.; Adeloju, S. B. *J. Chem. Educ.* **1993**, *70*, 258.

ABSTRACT

The design and use of a buret apparatus for CO_2 gas capture and mass determination are described. The derivation of a comprehensive equation to determine the CO_2 mass and percent carbonation of the material is outlined. Experimental factors such as temperature and pressure, including elevation effects, and apparatus parameters are discussed and incorporated into one general equation. The experimental system and calculations apply concepts of the ideal gas law and fluid mechanics. This approach, which may be adapted to the determination of the gas content of other gas evolving materials, uses relatively cheap and readily-available components in the chemistry laboratory.